

PATENT SPECIFICATION

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(54) ORGANIC COATING OF METALLIC SUBSTRATES

5 (71) We, JONES & LAUGHLIN STEEL CORPORATION, a Corporation organised and existing under the laws of the State of Pennsylvania, United States of America, of 3 Gateway Center, Pittsburgh, Pennsylvania 15230, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention generally pertains to a method of producing adherent organic coatings on a metallic substrate under vacuum and the product thereof. The method comprises applying at least two intermediate coatings on a metallic substrate prior to application of an organic layer. This procedure results in an adherent organic coating and an enhancement of the corrosion resistance of the coated substrate. All coatings, except an organic topcoat, are applied under pressures which are less than atmospheric pressure, in the method, a wire brushed substrate is first coated with a layer of vacuum vapor deposited zinc and then with at least one layer of a vacuum vapor deposited metal, alloy, inorganic compound or mixture thereof. Finally, a low volatility polymerizable organic primer coating is applied to the coated substrate while still under the influence of reduced pressure of vacuum. The organic coating is polymerized by radiation while still under the influence of vacuum.

15 In order to enhance corrosion resistance for exterior applications, steel strip is commonly coated with an organic compound such as paint, plastics or lacquer. Organic coatings commonly comprise a primer and a topcoat. A major percentage of such strip products are composed of hot dip galvanized material. Hot dip galvanized strip has proven to be

very difficult to process through coil coating lines because of poor macro-and micro-uniformity of the galvanized surface. Such surface nonuniformities often prevent the satisfactory performance of the necessary cleaning and inorganic pretreatment steps prior to paint application. In addition, even when galvanized strip has been satisfactorily processed through a coil coating line, corrosion resistance of the coated product is often unsatisfactory as a result of variable hot dip galvanized surface conditions. In any event, when contrasted with the hot dipped products, the product of the invention is characterised by superior organic adhesion and generally better but at least equivalent corrosion resistance in the primed and top coated state.

20 The principal basis for the above statement of comparative corrosion resistance properties resides in the results of salt spray tests. The tests were conducted upon steel substrates coated with layers of zinc, a barrier layer, a primer, and a heat curable topcoat. Topcoat formulations were generally a thermosetting acrylic resin. These samples were compared with hot dip galvanized samples, conventionally pretreated, primed with a heat curable epoxy primer and topcoated with the same thermosetting acrylic.

25 The coated panels were evaluated with respect to corrosion, blistering associated with corrosion, and loss of adhesion at scribed marks due to undercutting in a corrosive environment. Prior to testing two intersecting scribes were cut to the metal substrate on a portion of the surface of each specimen with a carbide-tipped tool. Salt Spray (Fog) Testing (ASTM Designation B 117—64) is an accelerated corrosion testing procedure. Inspections were made after 250, 500 and 1000 hours unless prior failure had developed.

30 The invention, up to and alternately

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including topcoating, is conducted entirely under vacuum in a continuous manner. This processing sequence is advantageous because two separate operations in existing technology, i.e. hot dip galvanizing and coil coating, are combined. Also, much greater control can be exerted over the process so that a uniform product with superior properties can be produced. The superior properties are a result of the fact that organic pretreatment is achieved simply by the controlled evaporation of a thin barrier layer which adheres with no difficulty to the previously deposited zinc coating. Thus, it can be seen that there is no requirement of cleaning and complex surface reactions with an aqueous solution as is the case for conventional processing of coated steel strip. The application and subsequent adhesion of the organic coating to the barrier layer is achieved with minimal difficulty because the surface composition and topography have been controlled through the steps of the vacuum vapor deposition of zinc and the barrier material.

It has been recently disclosed in United States Patent No. 3,674,445 that metallic substrates coated with vacuum vapor deposited zinc can be coated with an adherent organic coating. However, such product does not include a vacuum vapor deposited layer of a metal, alloy, or inorganic compound between the zinc and organic layers. This additional layer provides a barrier or chemical effect and results in improved corrosion resistance and equivalent organic adhesion characteristics when contrasted to the product of United States Patent No. 3,674,445.

As may be apparent from the foregoing description of the prior art, the product of the invention is superior to hot dip galvanized material from the standpoint of organic adhesion and superior to vacuum vapor coated material, from the standpoint of corrosion resistance. Thus, the product of the invention possesses a combination of the most desirable features of the prior art.

It is an object of the invention to provide a process in which strongly adherent organic coatings can be applied to metallic substrates.

It is a further object to conduct a process which provides strongly adherent organic coatings on metallic substrates entirely under vacuum.

It is an additional object to provide strongly adherent organic coatings upon a metallic substrate which has been successively coated with vacuum vapor deposited zinc and a barrier material.

It is an object of the invention to produce a strongly corrosion resistant organic coated product which is superior to that

produced by conventional hot dip galvanizing and coil coating as well as that produced by the direct application of an organic coating upon a vacuum vapor zinc coated metallic substrate.

Further features of the present invention will appear from the following description of the invention, reference being made to the accompanying drawings in which:

Figure 1 is a schematic illustration of one form of apparatus suitable for use in producing a product having an organic primer coating. As depicted by this Figure, a metallic coil, such as steel, is passed into an evacuated chamber, subjected to wire brushing, two vacuum vapor layer depositions, roll cooling, organic primer layer application, radiation polymerization, and passed from the evacuated chamber.

Figure 2 is a schematic illustration of one form of apparatus suitable for use in producing a product having organic primer and organic topcoat layers. As depicted by the Figure, a metallic coil is processed with the use of apparatus similar to that shown in Figure 1. However, the cured primer coated substrate is also coated with an organic topcoat layer and cured by radiation prior to passing from the evacuated chamber.

Figure 3 is a schematic illustration of another form of apparatus suitable for use in producing a product having organic primer and organic topcoat layers. As shown in this Figure, a metallic coil is processed with use of the same general apparatus that is shown in Figure 2. The difference is that the topcoat layer is applied and cured under atmospheric pressure upon exiting from the evacuated chamber.

Figure 4 is an illustration of a metallic substrate, such as steel, upon which four layers have been applied. The first two layers are vacuum vapor deposited zinc and a barrier material. The final two layers are an organic primer and organic topcoat.

Figure 5 is an illustration of a metallic substrate, such as steel, upon which five layers have been applied. The first layer is vacuum vapor deposited zinc and the second and third layers are vacuum vapor deposited zinc and the second and third layers are vacuum vapor deposited barrier material. The final two layers are an organic primer and organic topcoat.

The method of the present invention comprises the steps of passing a metallic substrate into an evacuated chamber, wire brushing at least one surface of the metallic substrate, vacuum vapor depositing a zinc layer upon the brushed surface of the metallic substrate, vacuum vapor depositing a thin barrier layer material of a metal, alloy, inorganic compound or a

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mixture thereof directly onto the surface of said zinc layer, applying a low volatility, polymerizable organic primer coating to the substrate of the coated metallic substrate, at least partially polymerizing said organic coating by subjecting said organic coating to radiation, and removing the organic coated substrate from said evacuated chamber.

The invention also provides a composite article of manufacture manufactured according to the above method and comprising a metallic substrate, a vacuum vapor deposited layer of zinc on said substrate, a vacuum vapor deposited barrier layer of a metal, alloy, inorganic compound or a mixture thereof on said zinc layer, and an adherent layer of a low volatility organic compound which is at least partially polymerized.

A suitable apparatus for applying an organic primer layer is schematically illustrated in Figure 1. Metallic strip 1 is passed through evacuated chamber 2 from uncoiling reel 4 and collected on coiling reel 5. Strip entry is accomplished by passage through seal rolls 6 and 7. Reel 5 is driven so as to continually move strip 1 at a desired rate of travel. Chamber 2 is evacuated through outlet 3 by means of a suitable vacuum pump, not shown. A suitable chamber vacuum level ranges from 5×10^{-5} mm Hg to 5×10^{-4} mm Hg. Upon entry into the chamber, the strip is mechanically abraded by a rotary wire brush 10 in order to abrasively clean the strip and to place it in a proper condition for subsequent vacuum vapor zinc deposition.

A pool of molten zinc is maintained in crucible 11 and heated to vaporization by appropriate means which may include an electron beam gun or resistance heater. A pool of molten barrier layer material is maintained in crucible 12 for vacuum vapor deposition upon the previously deposited zinc layer. Inorganic materials such as oxides may be conveniently vaporized through the electron beam bombardment of presintered oxide discs. Crucible 12 may also be heated by electron beam bombardment or a resistance heater. Roll 13 is arranged in such a manner that suitable roll cooling of the coated strip may be effected through contact with the roll surface. Although one roll is shown, it should be understood that one or more roll surfaces may be utilized. Roll cooling permits application of an organic coating. Application roll 14 is utilized to roller coat a layer of an organic compound onto the barrier layer. Roll 15 changes the pass line direction and finally, the organic coated strip is cured by radiation emitted by electron beam gun 16 before exiting from

chamber 2 through seal rolls 8 and 9. One or both sides of the strip may be coated through rearrangement of or additions to the above apparatus.

Figure 2 illustrates suitable apparatus for applying and polymerizing primer and topcoat organic layers within evacuated chamber 2. The primer is applied in the same fashion as in Figure 1. The organic topcoat is applied by reverse rollcoat application 17 and the direction of travel of strip 1 is changed by means of roll 18 in order to passover topcoat electron curing gun 19. The gun is typically operated at low voltages (<150 KV). After cutting or polymerizing the topcoat, the coated strip is passed from chamber 2 through seal rolls 8 and 9.

Figure 3 illustrates a suitable apparatus for applying and polymerizing primer and topcoat organic layers that is an alternative to the system shown in Figure 2. The primer layer is applied and polymerized in a similar manner, however, the topcoat layer is applied by reverse rollcoat applicator 20 at a location outside of evacuated chamber 2. After strip travel is changed in direction by roll 21, electron beam gun 22 is used to polymerize the topcoat under atmospheric pressure. The gun is typically operated at high voltages (>250 KV).

Upon entry into the evacuated system, the metallic substrate is mechanically abraided to the extent that an activated surface condition is obtained. Such surface condition will lead to the creation of a vacuum vapor deposited zinc layer having superior adherence. A suitable technique for activating the surface of metallic substrates is shown in British Patent No. 1,222,198.

Following surface preparation of the substrate, a layer of zinc is vacuum vapor deposited upon the substrate surface. This step may be accomplished by heating a liquid zinc containing source in vacuum and condensing the zinc vapors generated by the source upon the moving substrate. These steps, i.e. surface preparation and deposition, result in a zinc surface morphology that is generally smooth, clean, and free of adherence-offsetting second phases. The zinc surface has platelet texture which is very favorable for subsequent organic adhesion because of the creation of numerous locking sites on a micro-scale.

Vacuum vapor deposited zinc layers of a thickness greater than 2.5 microns develop a topographical texture of platelets which favor the subsequent excellent adhesion of organic compounds. In this regard, it has also been discovered that strip temperatures of at least 120°C at the completion of zinc vapor deposition also

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favor the development of a platelet texture which is sufficiently coarse to promote adhesion.

The barrier layer should be of a thickness which is controlled to be at least sufficient to cover the zinc layer but yet not of a thickness which will essentially change the favorable vacuum vapor deposited zinc surface morphology. As may be appreciated by those skilled in the art, the upper thickness range is thus a function of the particular zinc texture and; hence, can be expected to vary somewhat according to the zinc deposition practice followed in a given instance. While not diminishing the favorable effect upon subsequent organic adhesion, the barrier layer functions to markedly improve the corrosion resistance of the final product.

The barrier layer material comprises vapor deposited metal, alloy, inorganic compound or combination thereof. Exemplary materials include tin, aluminium, aluminium base alloys, aluminium-tin alloys, and silicon oxides. Silicon oxide coatings perform well when applied as an individual coating or as a second coating in combination with an initial aluminium coating.

Silicon oxide coating are applied by the evaporation of SiO_2 . The SiO_2 vapor becomes somewhat lean in oxygen during passage from the source to the substrate under the reduced pressures in the chamber. Thus, the deposited silicon oxide layer contains somewhat less than the stoichiometric amount of oxygen. Silicon oxide coatings of a thickness greater than 0.635 microns are not desirable. This is due to a substantial loss of organic adhesion which is because of brittleness which develops in silicon oxide layers greater than 0.635 microns thicknesses.

Following deposition of the barrier layer, the strip temperature may be adjusted through roll cooling. The purpose of this step is to adjust the strip temperature for application of a given organic formulation. It is to be understood that, in some instances, temperature adjustment may be unnecessary because the strip will inherently arrive at a suitable temperature without the need for roll cooling. Thus, this step is regarded as optional in the sense related above. Roll cooling may also advantageously be employed in order to reduce the time or travel space needed for the strip to cool to the desired coating temperature. In general, however, the processing of strip in vacuum systems is often limited because of the difficulty in extracting heat from the strip in lower temperature ranges where radiation cooling is not effective. Cooling by heat conduction from the strip to a heat sink such as a roll is often a necessary expedient.

In the context of this invention, roll cooling of a metallic strip which has been coated with zinc and a thin barrier layer may be rapidly cooled in a manner which does not appreciably disturb the surface morphology of the coated substrate and, as a consequence, does not interfere with the basic process and results described herein.

Roll cooling of the intermediately coated strip can be accomplished in an efficient manner. For example, a 68.5 cm diameter water-cooled turn-around roll (180° wrap) has been effective to reduce a strip temperature from about 230°C to about 65°C in less than two seconds. When continuous roll contact is not made because of poor strip shape and low strip tension, the majority of cooling will be due to radiation which is ineffective in this temperature range. In such instances it becomes necessary to employ high strip tension in order to ensure that strip having poor shape is pulled flat over the cooling roll and that good roll contact is made over the full width of the strip. It is also preferred that the cooling roll may be of as large diameter as practical and that the wrap angle be as large as possible. Both of the above features will maximize cooling due to increased contact times. The cooling roll should be smoothly finished to maximize contact with the coating protrusions and should also have sufficient water cooling from the roll interior to remove the heat transferred to the roll body from the strip. Also, the roll should be located to make the initial contact with the freshly deposited surface so that coating protrusions can be deformed to make good contact with the smooth roll surface.

The total amount of heat removal due to roll cooling can be monitored through measurement of water flow and inlet and outlet water temperatures. With a knowledge of strip speed, gauge, width, and initial strip temperature, the strip temperature upon roll cooling can be calculated. Such calculation thus permits control of final strip temperature to be achieved through the use of controlled water inlet temperature to the cooling roll interior.

Following roll cooling or vacuum vapor deposition of the barrier layer, as the case may be, the substrate is coated with a low volatility organic material while still under the influence of vacuum. Application of the coating while still under vacuum offers the advantage that there can be no contamination of the strip other than possible gas absorption. On the other hand, the application of organic materials in environments outside of the vacuum

chamber obviously increases the risk that harmful contamination will occur.

At this stage in the process, the preparation of the intermediate product has been carefully controlled in such a manner that a product having superior organic coating adhesion and corrosion properties may be obtained. The preparation of the coated substrate for application of the organic material has been controlled from two standpoints. First of all, the coated surface morphology is of the desired platelet topography. Secondly, temperature of the strip is controlled to allow for flow and leveling of the organic material on a macroscale across the vapor deposited surface while the vacuum environment allows unimpeded flow between the platelet texture on a microscale. This set of conditions ensures superior organic adhesion and superior corrosion resistance when the coating layer is subsequently polymerized.

A preferred organic primer thickness range is from 4.5 to 7.5 microns and thickness ranging from 3.8 to 10.2 microns are generally suitable. As the barrier coated zinc platelet peaks are generally on the order of 3.8 microns in height, this amount of organic thickness is usually necessary to satisfy the porosity of the coated substrate and to cover the surface up to the peaks. Hence, minimum thickness should be approximately 4.5 microns in order to ensure that the substrate is adequately coated with the organic material so as to ensure the attainment of superior corrosion properties. On the other hand, corrosion resistance does not appreciably improve at primer thicknesses of over 7.5 microns and there is little advantage in producing primer coatings above this thickness value. Primer coatings are generally applied in thickness of about 6.35 microns.

Roller coating is a satisfactory method for application of the organic coating. This general type of coating technique is conventionally utilized for coating moving substrates and need not be described further. Other methods such as extrusion, curtain or powder coating are also applicable for use in this invention.

After application, the organic layer is polymerized in place by exposure to radiation such as electron beam or ultraviolet radiation. Polymerization is accomplished while the coated strip is still within the evacuated chamber since low beam voltages can be used to advantage. Radiation curing or polymerization of organic coated materials is known in the art. Illustrative patents which discuss this technique include United States Patent No. 3,547,683 and British Patent Nos. 801,479 and 949,192. As radiation polymerization is

a conventional technique, no further discussion of this step is believed to be necessary.

For a coil coated product to be of maximum utility, it should contain both primer and topcoat organic layers. Primer coats usually contain an inhibitive pigment which chemically aids in suppressing underfilm corrosion and may be formulated to maximize adhesion to the substrate. Primers of the preferred thickness generally have poor hiding ability as well as poor resistance to the degrading effects of sunlight. Thus, in order to achieve reproducible color coatings which are not dependent upon substrate and primer coloration, a topcoat is required. Topcoat thicknesses generally are greater than 17.8 microns and are, preferably, on the order of 25.4 microns in order to obtain complete hiding of the substrate color. Topcoats generally have higher pigment contents than primers and thus are superior with regard to hiding and resistance to the degrading effects of sunlight and moisture. Topcoats should also be deformable and exhibit good adhesion to the primer coating. In order to obtain good forming properties, the majority of coil coating topcoats have thicknesses no greater than about 25.4 microns.

A rather wide range of topcoat formulations are suitable for the practice of the invention. Such formulations include both conventional and heat curable topcoats such as acrylic resins polyesters, siliconized acrylic resins and polyesters, polyfluorocarbons, as well as electron beam curable acrylic resins. At this juncture, it is pointed out that the application of the topcoat layer over the primer may be accomplished in three ways. They are: (1) application and curing under vacuum, (2) application in line after strip exit from the vacuum chamber and curing with an atmosphere electron beam apparatus, and (3) application and curing by conventional means in a separate facility.

During the vacuum application and curing of topcoats, such as illustrated in Figure 2, the previously applied primer coating is subjected to very light electron beam radiation prior to topcoat application. This procedure is followed so that the topcoat can be applied over a primer which is cured to the degree that mixing of the respective organic layers does not occur. The undercured primer, however, provides for good intercoat adhesion. Because the topcoat is applied in thicknesses greater than the primer and with a uniform smooth surface, reverse roll coating is a preferred application technique. Other methods such as curtain or extrusion coating are feasible but are

considered to be relatively more difficult to conduct under vacuum. Curing of the topcoat may be accomplished by a low voltage (<150KV) electron beam. Complete curing of the primer and topcoat are simultaneously effected at this stage of the process.

In contrast with topcoat application and curing under vacuum, primer coating should be cured to a greater degree when in-line application of the topcoat after exit from the evacuated chamber is used. This is because the primer requires a considerably greater degree of curing to enable it to be passed through the seal rolls. Once the prime coated material exits from the evacuated chamber, the topcoat layer is applied by reverse roll coating and curing is effected by electron beam curing at high voltages (>250 KV). Such application and curing techniques are conventional. As in the case of the process embodiment in which topcoat application and curing was conducted under vacuum, full curing of the primer and topcoat would be accomplished simultaneously. Although one could consider the possibility of placing a conventional heat curing topcoat system in-line with the vacuum system to produce a fully coated product, process control would be quite difficult due to the necessity to balance the slower line speed of the topcoat curing system with the faster line speed of the vacuum system. This factor is not significant when an electron beam topcoat curing system is employed.

For out-of-line topcoat application and curing, the vacuum primed coated substrate is fed into conventionally available solvent-containing heat-curable topcoat facilities. No cleaning or phosphating facilities are necessary.

A suitable primer material for use in the invention should be of a low volatility to be applied under vacuum environment and should also be capable of polymerization under radiation such as electron beam or ultraviolet radiation. Such organic materials include acrylic resins, epoxy resins, and siliconized versions of these resins. An acrylic ester is a preferred resin.

As can be seen from the above discussion of the process, there are a wide range of variables relating to the invention. The following specific conditions were found to be suitable for obtaining a highly adherent and corrosion resistant primer coating of an acrylic ester.

Upon surface activation by wire brushing, the vacuum vapor deposited zinc layer should be greater than about 2.54 microns in thickness in order to develop a surface morphology of platelets favorable for organic adhesion. In connection with this requirement, strip temperatures about 120°C at the completion of zinc vapor deposition also favor the development of platelet texture which is sufficiently coarse to promote adhesion.

Coating performance is enhanced by the vacuum vapor deposition of a thin aluminium layer directly upon the previously deposited zinc layer. The aluminium layer should be of 0.25 to 0.50 microns in thickness. Although not quite as effective in promoting adhesion as the aluminum layer, a 0.38 to 0.63 microns layer of silicon oxide deposited from a source of SiO₂ performs satisfactorily either as a substitute layer for aluminium or as an additional layer which is vapor deposited over the aluminium layer.

A strip temperature range which is preferred for roller coating of acrylic esters is between 65°C and 120°C. This temperature range is suitable to ensure that organic deposition and levelling will properly take place prior to curing. Roll cooling of the strip is necessary to obtain proper strip temperature in this instance. For the application of acrylic ester coatings in the thickness range of 3.8 to 10.2 microns it is suitable to heat the organic formulation to approximately 77°C in order to obtain the desired viscosity for flow-out and levelling.

A specific example of the process as applied to a 30 cm wide strip of low carbon steel is described below. The 0.045 cm thick strip was passed through an evacuated chamber at a speed of 30 m/min.

A dry, cleaned strip having a temperature of 55°C was passed into an evacuated chamber. The strip entry temperature was due to heat retained from the cleaning bath.

The strip was then wire brushed with a brush driven at 7 amps by a no load 500 RPM, 440-volt, three-phase motor. Brush rotation was counter-current with the direction of strip travel. Strip temperature increased from 55°C to 105°C due to brush friction.

A 15.2 micron layer of zinc was vacuum vapor deposited upon brushed strip. A graphite resistance heated source was employed. This procedure resulted in a strip temperature increase to 220°C.

An 0.50 microns layer of aluminium was vacuum vapor deposited upon the zinc layer. An electron beam heated source was utilized. This procedure resulted in a temperature increase to 230°C.

The coated strip was then passed around a 68 cm diameter water cooled roll as a wrap angle of 180°. Contact time was 2 seconds. This resulted in a reduction of strip temperature from 230°C to 65°C.

A 6.3 microns coating of an acrylic ester was applied to the coated strip by direct roll coating of about 65°C.

Finally, the coated strip was cured or polymerized with the use of radiation emitted from a 150 KV, 10 mA electron beam generator which scanned the strip at 100 cycles/second.

WHAT WE CLAIM IS:-

1. A method of producing an adherent organic coating on a metallic substrate under vacuum characterized in comprising:
 - a. passing a metallic substrate into an evacuated chamber;
 - b. wire brushing at least one surface of the metallic substrate;
 - c. vacuum vapor depositing a zinc layer upon the brushed surface of the metallic substrate;
 - d. vacuum vapor depositing a thin barrier layer material of a metal, alloy, inorganic compound or a mixture thereof directly onto the surface of the said zinc layer;
 - e. applying a low volatility, polymerizable organic primer coating to the substrate of the coated metallic substrate;
 - f. at least partially polymerizing said organic coating by subjecting said organic coating to radiation; and
 - g. removing the organic coated substrate from said evacuated chamber.
2. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that said vacuum vapor deposited layer of zinc is at least 2.5 microns in thickness.
3. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 2, characterized in that the metallic substrate is at a temperature of at least 120° upon completion of zinc vapor deposition.
4. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that it further includes the step of: controlling the thickness of said barrier layer within a thickness range which is sufficient to cover the zinc layer to that in which the zinc layer surface morphology is not essentially changed.
5. A method of producing an adherent organic coating on metallic substrate under vacuum according to claim 4, characterized in that said barrier layer comprises aluminium.
6. A method of producing an adherent organic coating on metallic substrate under vacuum according to claim 4 characterized in that said barrier layer comprises silicon oxide.
7. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 5 characterized in that it further includes the steps of vacuum vapor depositing a second barrier layer material of silicon oxide directly over said aluminium barrier layer.
8. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 5, characterized in that said aluminium barrier layer is 0.25 to 0.50 microns in thickness.
9. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 6, characterized in that said silicon oxide barrier layer is 0.38 to 0.63 microns in thickness.
10. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 7, characterized in that said aluminium barrier layer is 0.25 to 0.50 microns in thickness and said silicon oxide layer is 0.38 to 0.63 microns in thickness.
11. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that said organic coating is an acrylic, epoxy, siliconized acrylic or epoxy resin or a mixture thereof.
12. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 11, characterized in that said acrylic resin is an acrylic ester.
13. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1 characterized in that it further includes the step of: lowering the temperature of the coated metallic substrate prior to applying said organic coating.
14. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 13, characterized in that said temperature adjustment is effected by cooling said coated metallic substrate by contact with a surface of a roll.
15. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that said organic coating is applied by roller coating.
16. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that it further includes the steps of: applying a polymerizable organic topcoat coating on said at least partially polymerized organic primer coating and polymerizing said organic topcoat coating and completing any remaining polymerization of said organic primer coating.
17. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1,

characterized in that said organic coating is polymerized by the application of electron beam radiation.

18. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that said organic coating is polymerized by the application of ultraviolet radiation.

19. A method of producing an adherent organic coating on a metallic substrate under vacuum according to claim 1, characterized in that said metallic substrate comprises steel.

20. A composite article of manufacture manufactured according to the method described in any one of claims 1—19 characterized in comprising:

- a. a metallic substrate;
- b. a vacuum vapor deposited layer of zinc on said substrate;
- c. a vacuum vapor deposited barrier layer of a metal, alloy, inorganic compound or a mixture thereof on said zinc layer; and
- d. an adherent layer of a low volatility organic compound which is at least partially polymerized.

21. A composite article of manufacture according to claim 20, characterized in that said zinc layer has a platelet texture and is of a thickness of at least 2.5 microns.

22. A composite article of manufacture according to claim 20, characterized in that said barrier layer ranges from a thickness which is sufficient to cover the zinc layer to a thickness in which the zinc layer surface morphology is not essentially changed.

23. A composite article of manufacture according to claim 22, characterized in that said barrier layer comprises aluminium.

24. A composite article of manufacture according to claim 22, characterized in that said barrier layer comprises silicon oxide.

25. A composite article of manufacture according to claim 23, characterized in that said aluminium barrier layer is from 0.25 to 0.50 microns in thickness.

26. A composite article of manufacture according to claim 23, characterized in that said silicon oxide barrier layer is 0.38 to 0.63 microns in thickness.

27. A composite article of manufacture according to claim 23, characterized in that it further includes;

- a second vacuum vapor deposited barrier layer comprising silicon oxide on said aluminium barrier layer.

28. A composite article of manufacture according to claim 27, characterized in that said aluminium barrier layer is from 0.25 to 0.50 microns in thickness and said silicon oxide barrier layer is from 0.38 to 0.63 microns in thickness.

29. A composite article of manufacture according to claim 20, characterized in that it further includes:

- a second organic layer superimposed on the organic layer, both organic layers being polymerized.

30. A composite article of manufacture according to claim 20, characterized in that said at least partially polymerized organic compound comprises an acrylic, epoxy, siliconized acrylic or epoxy resin, or mixtures thereof.

31. A composite article of manufacture according to claim 30, characterized in that said at least partially polymerized organic compound comprises an acrylic ester.

32. A composite article of manufacture according to claim 20 characterized in that said metallic substrate comprises steel.

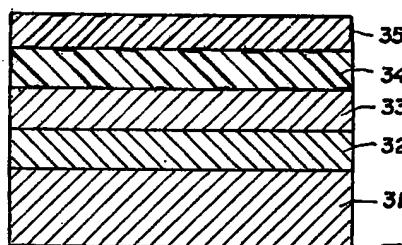
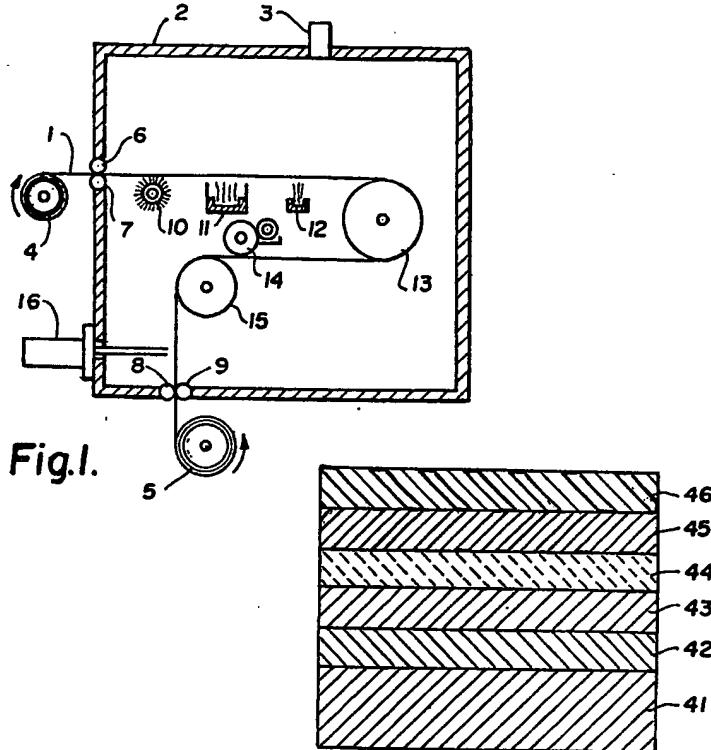
33. A composite article of manufacture according to claim 20, characterized in that said at least partially polymerised organic layer is of a thickness from 3.8 microns to 10.2 microns.

34. A composite article of manufacture according to claim 31, characterized in that said at least partially polymerised acrylic ester coating is of a thickness of from 5.0 to 7.6 microns.

35. A composite article of manufacture according to claim 34, characterized in further comprising a polymerized layer of an organic compound consisting of an acrylic resin, a polyester, a siliconized version of an acrylic resin or polyester, or a mixture thereof, the layer being of a thickness of at least 17.8 microns.

GERALD CARTER & COMPANY
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Agents for the Applicants

1471977 COMPLETE SPECIFICATION
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Sheet 1



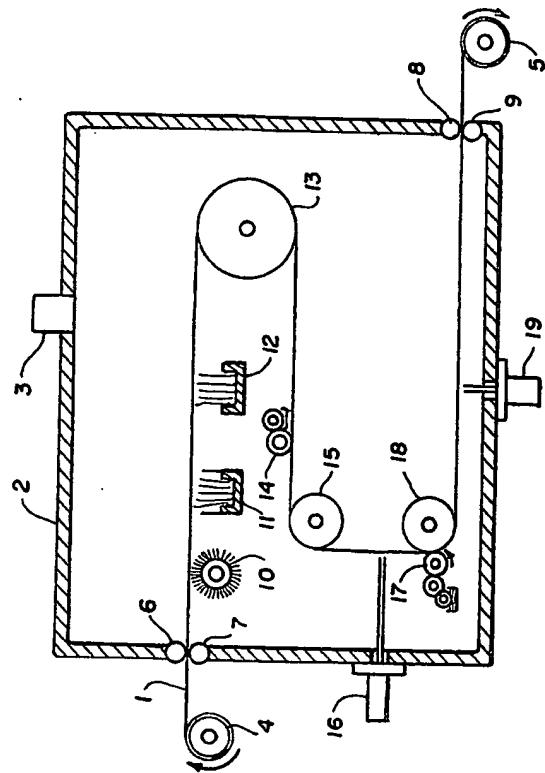


Fig. 2.

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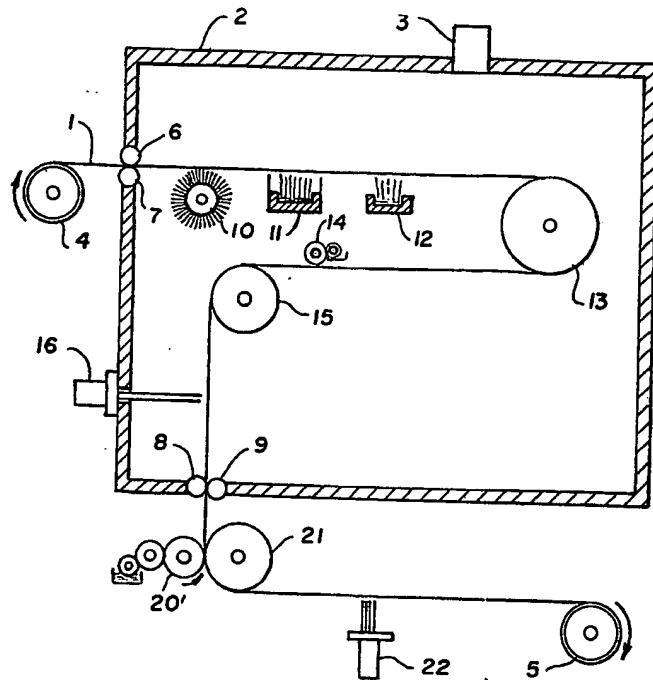


Fig. 3.